

## Isotopic characterization of a depleted uranium plume and source

Bradley K. Esser<sup>1</sup>, Alan Volpe<sup>1</sup>, Ross Williams<sup>1</sup>, Michael Taffet<sup>2</sup>, and Eric Christofferson<sup>2</sup>

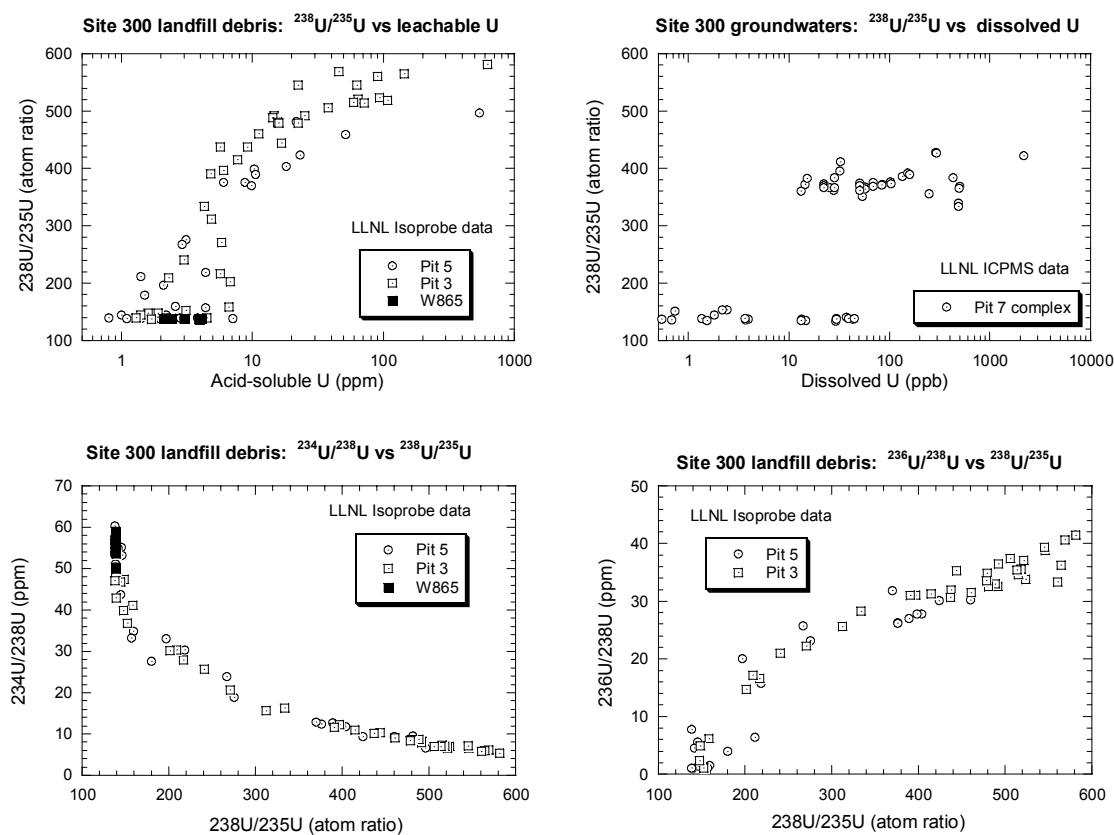
<sup>1</sup> Analytical & Nuclear Chemistry Division (L-231), Lawrence Livermore National Laboratory, Livermore, CA, 94551-0808 ([bkesser@llnl.gov](mailto:bkesser@llnl.gov))

<sup>2</sup> Environmental Restoration Division (L-530), LLNL, Livermore, CA, 94551-0808

Uranium contamination in soil and groundwater is a widespread problem within the DOE and DoD complex. Associating U contamination with a specific source and then mapping the distal edge of the plume or contamination area is often difficult, but is vital to understanding fate and transport, to designing a viable remediation strategy, and to assigning CERCLA liability. Groundwaters associated with sedimentary rocks high in organic material often have total U activities in excess of drinking water standards; in areas with complex geology, this can complicate the use of U concentration alone to distinguish between natural and anthropogenic uranium. In other areas, multiple sources of anthropogenic U may exist. Ketterer et al. (2000) describe a river site with potential inputs of depleted and enriched U from a uranium metal processing plant and of anthropogenic U of natural isotopic composition from an ilmenite processing plant.

The problem of determining U provenance and mapping anthropogenic U plumes is exacerbated by the use of standard EPA protocols for determining U activity in groundwater by alpha counting. The primary distinction between enriched or depleted anthropogenic uranium and natural uranium is the isotopic abundance of <sup>235</sup>U, which is invariant in natural U and which is difficult to accurately and precisely assess with alpha counting. The other unambiguous marker for anthropogenic uranium is the presence of non-naturally occurring <sup>236</sup>U at low levels in both enriched and depleted uranium. Inductively-coupled plasma mass spectrometry is capable of precisely and accurately determining U isotopic composition, including <sup>236</sup>U, in groundwaters and soils. We report <sup>234</sup>U, <sup>235</sup>U, <sup>236</sup>U abundances in soils and groundwaters contaminated with depleted uranium, and use this data to understand the process by which depleted uranium enters the groundwater system.

Site 300 is a DOE test range operated by Lawrence Livermore National Laboratory in the Altamont Hills about 65 miles southeast of San Francisco. Historically, LLNL has conducted high explosives tests on gravel-lined firing tables. From 1963 to 1988, firing table gravels which were contaminated with depleted uranium, lead and tritium (Lamarre and Taffet, 1989), were excavated on a semiannual basis and placed in shallow, unlined landfill pits. In 1988, LLNL changed operational procedures to minimize the generation of mixed waste, and excavated all firing table gravels and contaminated soils to Pit 7. The Pit 7 Complex sits in a small valley and includes Pits 3 and 5 which were closed before 1980. In 1992, an impermeable clay cap was placed over Pit 7 and part of Pit 3. A perched alluvial aquifer underlies the landfills, and in wet El Nino years (e.g. the winter of 1997-98), the pits become inundated by the rising water table. Site 300 and the Pit 7 Complex support a dense network of monitoring wells. In this report, we discuss data from wells in the Pit 7 Complex, with emphasis on NC7-48, a well completed in the alluvial aquifer immediately downgradient from Pit 7.

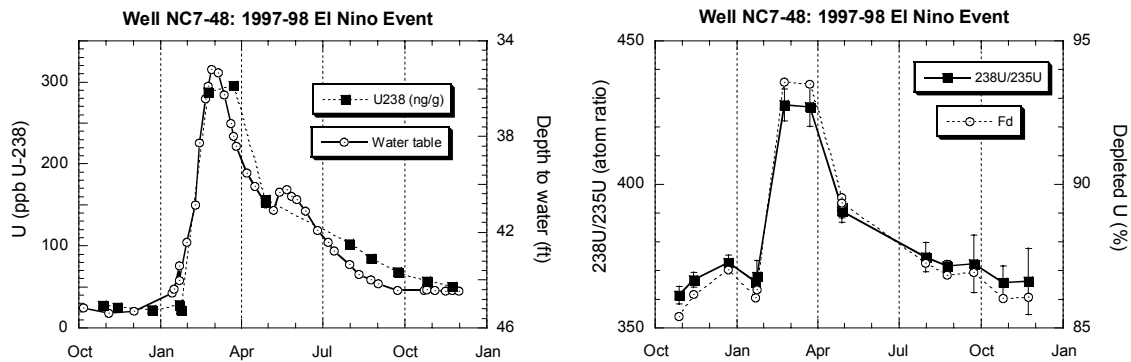


**Figure 1.** Isotopic composition of uranium in LLNL Site 300 groundwater and landfill debris

The Analytical & Nuclear Chemistry Division at LLNL has recently acquired a high-resolution, multi-collector ICPMS (Micromass Isoprobe). We have used this instrument to characterize U in 73 landfill debris samples collected from Pits 3 and 5 and from an uncontaminated site (W865). A fine fraction was collected from each sample, and leached in strong nitric acid. After spiking with  $^{233}\text{U}$ , leachate was passed through an anion exchange column and leachable U concentration was determined by isotope dilution. Uranium isotopic composition was determined by simultaneous collection of  $^{238}\text{U}$ ,  $^{235}\text{U}$  and  $^{233}\text{U}$  on Faraday cups and  $^{234}\text{U}$  or  $^{236}\text{U}$  on a pulse-counting Daly detector.

The U isotope systematics in landfill debris are quite consistent (Figure 1). Debris from the uncontaminated site (W865), and a number of samples from the landfills contain low concentrations of U, natural  $^{235}\text{U}/^{238}\text{U}$ , close to secular equilibrium  $^{234}\text{U}/^{238}\text{U}$ , and no  $^{236}\text{U}$ . The samples containing the highest concentrations of U have the most depleted  $^{235}\text{U}$  and  $^{234}\text{U}$  abundances, and contain  $^{236}\text{U}$ . The anthropogenic endmember in Pit 3 appears to be more depleted in  $^{235}\text{U}$  and  $^{234}\text{U}$ , and to contain higher levels of  $^{236}\text{U}$  than the endmember in Pit 5. All other samples are simple mixtures of natural and depleted uranium.

Since 1993, waters from monitoring wells at Site 300 have been analyzed by single-collector quadrupole ICPMS (VG Plasmaquad and HP4500) for uranium concentration and isotopic composition. The water data for the Pit 7 complex are shown in Figure 1. One obvious feature is the overlap in concentration between samples with natural and depleted signatures. In Pit 7 wells,



**Figure 2:** Pit 7 monitoring well NC7-48, El Nino winter of 1997-98. a) U concentration and water table level, b)  $^{238}\text{U}/^{235}\text{U}$  atom ratio and depleted U fraction

a number of waters with U activity below the drinking water standard contain predominantly depleted U. In other Site 300 groundwaters, we have found evidence for depleted U in waters with sub-ppb total U concentrations. Conversely, up-, cross-, and distal downgradient Pit 7 waters may contain U activity greater than the drinking water standard and have an entirely natural U isotopic composition. Only proximal downgradient wells show evidence of depleted U. These waters also contain  $^{236}\text{U}$  and are depleted in  $^{234}\text{U}$ .

Uranium data from a single well demonstrates the mechanism by which depleted uranium enters the groundwater system. The wet El Nino winter of 1997-98 caused the water table of the perched alluvial aquifer underlying the Pit 7 Complex to rise into the landfills. At NC7-48, a well immediately downgradient of Pit 7, U concentration rose by two orders of magnitude in concert with groundwater elevation rise. Uranium in the well also became more depleted, indicating a higher fraction of landfill U. The extremely rapid rise in uranium indicates that some fraction of the depleted uranium in the landfills is readily soluble. We are just beginning studies at LLNL into the use of permeable reactive barriers to immobilize uranium from slug releases associated with El Nino.

The use of mass spectrometry offers a number of advantages for the characterization of anthropogenic U. The ability to precisely characterize  $^{235}\text{U}$ ,  $^{234}\text{U}$  and  $^{236}\text{U}$  at environmental levels allows unambiguous attribution of groundwater U provenance. In areas affected by anthropogenic U with natural, depleted, and enriched isotopic composition, the use of 4 isotopes will allow the contributions of each component to be quantified.

## References

- Ketterer M. E., Wetzel W. C., Layman R. R., Matisoff G., and Bonniwell E. C. (2000) Isotopic studies of sources of uranium in sediments of the Ashtabula River, Ohio, USA. *Environ. Sci. Tech.* **34**(6), 966-972.
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